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Calorimetric Evidence for Pauli-Paramagnetic Superconductivity

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Specific-heat measurements at $0 \leq H \leq 29$kG, $0.33 \leq T/T_c \leq 1$, on the extreme ($\kappa_G \approx 67$) type-II superconducting alloy Ti-16 at.% Mo (previously shown to display reversible paramagnetic magnetization in the superconducting mixed state) (1) confirm the second-order nature of the upper-critical-field transition between the paramagnetic mixed and paramagnetic normal states at $H_u(T)$ down to $T/T_c = 0.76$, (2) show that the mixed state remains a single thermodynamic phase in the paramagnetic region, and (3) indicate that $\kappa_1 \equiv H_u/\sqrt{2}H_c$ and $\kappa_2 \propto \{\partial[4\pi(M_S - M_N)]/\partial H\}_{H_u}^{-1/2}$ (where H_c is the thermodynamic critical field, and M_S and M_N are superconducting mixed-state and normal-state magnetizations), both decrease with decrease of T.

WE report specific-heat measurements made in applied fields $0 \leq H \leq 29$ kG at $1.4 \leq T \leq 5$°K on the extreme type-II superconducting alloy Ti-16 at.% Mo. This very "dirty" or short electron-mean-free-path material is characterized by an unusually high Ginzburg-Landau parameter ($\kappa_G \approx 67$), as calculated from the Gor'kov-Goodman formula. Recent magnetization measurements[1–3] have shown that Ti-16 at.% Mo, and other alloy superconductors with $30 < \kappa_G < 100$, exhibit reversible *paramagnetic* magnetization in the high-magnetic-field superconducting mixed state. No apparent discontinuity was observed[1–3] at the upper critical field $H_u(T)$ where the paramagnetic superconducting- and normal-state magnetizations become equal, implying a second-order-type superconducting-to-normal-state transition. Relevant to these measurements are recent theories[4,5] which consider the enhancement of Pauli paramagnetism in the mixed state by spin-orbit-coupling–induced electronic spin-flip scattering. In view of the magnetization measurements[1–3] and the relevant theories[4,5] a calorimetric study of the superconducting and normal-state characteristics of Ti-16 at.% Mo is of special interest.

Figure 1 shows the specific-heat data for an annealed,[1] homogeneous, arc-melted button of Ti-16 at.% Mo. The apparatus, technique, and data reduction are essentially the same as previously described.[6] Magnetic fields were generated by a 3-in.-i.d. copper-coated Nb-Zr wire superconducting Helmholtz-pair solenoid with a field homogeneity of better than ±0.1% over the specimen volume. The data of Fig. 1 show relatively sharp ($\Delta T \approx 0.1$°K) bulk specific-heat jumps ΔC in both zero and large applied magnetic fields. The nearly discontinuous nature of the specific-heat jumps, and, in addition, the close agreement at equal (H,T) points with different (H,T) histories (see figure caption) confirms that the transitions are of second-order type and show that the mixed state remains a single thermodynamic phase in the paramagnetic region, in accord with the magnetization measurements.[1–3] The relatively narrow transition widths are surprising in view of the very short calculated[7] superconducting-state coherence distance $\xi_G \approx 55$ Å and the resulting possibility[8] of ≈ 0.5°K thermal-fluctuation broadening.

In the normal state above the specific-heat jumps, the data follow the usual relationship: $C_n = \gamma T + \beta T^3$. Although not apparent in Fig. 1, a monotonic decrease (probably instrumental) of both γ and Θ_D with increase of H ($\approx 6\%$ in $\Theta_D \propto \beta^{-1/3}$ and $\approx 3\%$ in γ at $H = 29$ kG) is observed. From the $H = 0$ data we obtain (1) the normal-state electronic-specific-heat coefficient $\gamma = 7.67 \pm 0.04$ mJ/mole(°K)$^2 \approx 7520$ ergs/cm^3(°K)^2 with $V \approx 10.2$ cm^3/mole [hence $\kappa_G \approx 7500\ \gamma^{1/2}\rho_n = 67$ with $\rho_n(4.2) = 1.03 \times 10^{-4}$ohmcm, and the Maki parameter $\alpha^2 \approx 5.6\rho_n^2\gamma^2 = 3.4$]; (2) the Debye temperature $\Theta_D = 302 \pm 10$°K; (3) the specific-heat jump[9] $\Delta C(T_c) = 1.65\gamma T_c$; (4) the superconducting-state electronic specific heat[9] $C_{es} = 8.32\gamma T_c \exp(-1.50T_c/T)$ for $3 \gtrsim T_c/T \gtrsim 1.8$; (5) the thermodynamic critical field[9] $H_c(T) = H_{c0}$

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[1] R. R. Hake, Phys. Rev. Letters **15**, 865 (1965).

[2] J. A. Cape, Phys. Rev. **148**, 257 (1966).

[3] R. R. Hake, in Proceedings of the Tenth International Low Temperature Conference, 1966 (to be published).

[4] K. Maki, Phys. Rev. **148**, 362 (1966).

[5] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).

[6] R. R. Hake, Phys. Rev. **123**, 1986 (1961); R. R. Hake and W. G. Brammer, *ibid*. **133**, A719 (1964).

[7] We employ the Ginzburg-Landau coherence distance $\xi_G \approx (\xi_0 l)^{1/2} = 1.0 \times 10^{-6}(\rho_n\gamma T_c)^{-1/2}$, where ξ_0 is the BCS coherence length, l is the electron mean free path, and units are ρ_n (ohm cm) and γ [erg/cm^3 (°K)^2]. The sharpness of the present zero-field transition may be consistent with the suggestion of C. Caroli, P. G. de Gennes, and J. Matricon [Physik Kondensierten Materie **1**, 176 (1963)] that $\xi_G \to \infty$ as $t \to 1$ in accord with $\xi_G \approx 0.85 (\xi_0 l)^{1/2}(1-t)^{-1/2}$, where $t \equiv T/T_c$.

[8] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950); B. B. Goodman, J. Phys. Radium **23**, 704 (1962).

[9] According to the BCS theory [see J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 170] $\Delta C\ (T_c) = 1.43\ \gamma\ T_c$, $C_{es} = 8.5\gamma T_c \exp(-1.44T_c/T)$ for $2.5 < T_c/T < 6$, and $|D(T)|_{max} \approx 0.036$ (negative).

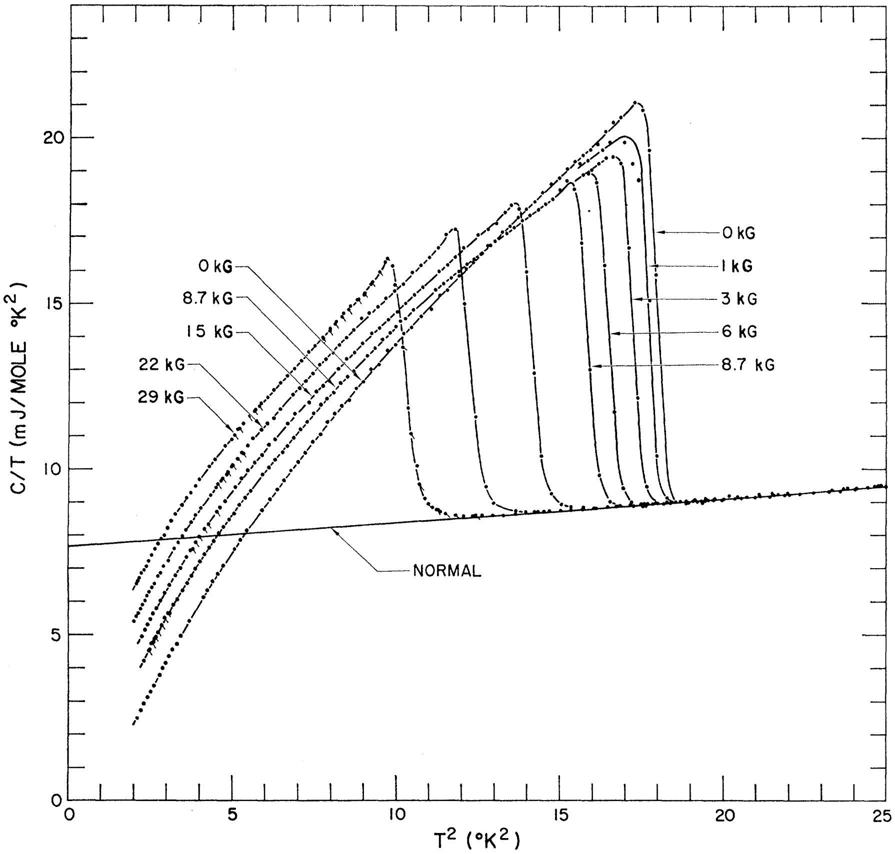

FIG. 1. Specific heat C of annealed Ti-16 at.% Mo plotted as C/T versus T^2. All data were taken at constant H and increasing T. Data (solid circles) for $H=0$ represent the virgin sample prior to magnetic field application. Data (solid circles) for $H=8.7$, 15, 22, 29 kG were taken after applying H in the normal state at about 5°K and then cooling via a mechanical heat switch to 1.4°K in the field. Data (solid circles) for $H=1$, 3, 6 kG were obtained similarly; however, these measurements spanned only the transition regions. The data represented by solid circles with ticks were taken at $H=8.7$, 15, 22, and 29 kG in succession after cooling to 1.4°K in zero field. Note the (H,T) history independence of the C/T data and the peculiar pre-transition peaks.

$\times[1-(T/T_c)^2]+D(T)H_{c0}$, where $H_c(0)\equiv H_{c0}=0.905$ kG, $H_c(T=T_c=4.246°\text{K})=0$, and $|D(T|)_{\max}=0.02$ (negative). The indicated uncertainties in γ and Θ_D are probable errors derived from a least-squares analysis.

Figure 2 shows that the calorimetrically determined (H_u,T_s) boundary is in reasonably good agreement with previous magnetization and resistive determinations[1–3] of $H_u(T)$ on different specimens of Ti-16 at.% Mo. The apparent differences between the T_c values of the calorimetric and different magnetization specimens ($\Delta T_c \lesssim 0.15$°K) shown on Fig. 2 may be due to slightly different alloy or interstitial-gas concentrations. All caloric, magnetization,[1–3] and resistive[1,3] measurements agree that the (H_u,T_s) boundary is well above the magnetically[1–3] determined paramagnetic superconductivity onset field $H_{ps}(T)$. As previously discussed[1] the *second-order* nature of the boundary implies that the high-field mixed state must be characterized by a Pauli-paramagnetic conduction-electron spin alignment which is comparable to that in the high-field normal state regardless of other possible contributions to superconducting and normal-state magnetizations.

TABLE I. Superconducting transition characteristics of Ti-16 at.% Mo.

H_u[a] (kG)	T_s[b,c] (°K)	ΔC[c] (mJ/mole°K)	H_e[d] (G)	$(\partial H_u/\partial T)_{T_s}$[e] (kG/°K)	Calorimetric κ_1[f]	κ_2[g]
0	4.246	53.8	0	34.1	61	...
0.99	4.212	49.1	14	33.8	...	58
2.99	4.159	46.2	35	32.8	60	58
5.99	4.067	43.6	71	32.3	60	58
8.76	3.980	41.6	103	31.3	60	57
14.99	3.772	37.6	179	28.6	59	54
22.01	3.509	33.8	271	25.2	57	48
29.04	3.216	29.3	368	23.7	56	46

[a] Measured upper critical field.
[b] Measured superconducting-transition temperature.
[c] The transition temperature T_s and the corresponding specific heat jump $\Delta C(T_s)$ are determined by extrapolation of pre- and post-transition C/T-versus-T curves into the transition region so as to intersect a line normal to the T axis through T_s, thus describing an idealized zero-width transition. T_s is chosen near the transition midpoint such that the total area (entropy) under the actual C/T-versus-T curve is preserved by the idealized curve.
[d] Thermodynamic critical field from double integration of $C_s(H=0)/T$ and $C_n(H=0)/T$.
[e] Obtained by graphical differentiation of the calorimetric $H_u(T)$ curve.
[f] Using $\kappa_1(T)=H_u/\sqrt{2}H_c$ except for $\kappa_1(T_c)$ which is obtained from Eq. (1).
[g] From Eq. (2).

Table I lists the calorimetrically determined superconducting-transition characteristics of Ti-16 at.% Mo, including parameters κ_1 and κ_2. At T_c the expression $\kappa_1(T_c)=(\partial H_u/\partial T)_{T_c}/\sqrt{2}(\partial H_c/\partial T)_{T_c}$ can be combined with the Rutgers relationship $\Delta C(T_c)=(VT_c/4\pi)\times(\partial H_c/\partial T)^2_{T_c}$ to obtain

$$\kappa_1(T_c)=(\partial H_u/\partial T)_{T_c}[VT_c/8\pi\Delta C(T_c)]^{1/2}. \quad (1)$$

For the present case $\kappa_2 \gg 1$, and thus $\kappa_2\equiv(2\delta S)^{-1/2}$, where $S\equiv[\partial 4\pi(M_S-M_N)/\partial H]_{H_u}$, M_S and M_N are the superconducting and normal-state magnetizations, and $\delta=1.16$ for a triangular vortex lattice.[10] Using the Ehrenfest relation $\Delta C(T_s)=(VT_sS/4\pi)(\partial H_u/\partial T)^2{}_{T_s}$ one obtains[11]

$$\kappa_2(T_s)=(\partial H_u/\partial T)_{T_s}[VT_s/8\pi\delta\Delta C(T_s)]^{1/2}. \qquad (2)$$

The calorimetric κ_1 and κ_2 values both *decrease* with decrease of T in qualitative accord with magnetization measurements[2,3] and recent theory.[4,5] Detailed comparison of the various experimental and theoretical κ_1 and κ_2 values will be reserved for a later publication.[12]

In conclusion we believe that the present specific-heat results establish the reality of high-field Pauli-paramagnetic superconductivity in the mixed state of extremely "dirty" type-II superconducting alloys. It should be of some interest to examine the extent and nature of Pauli paramagnetism in the mixed state of "clean" or intrinsic high-κ type-II superconductors.[13]

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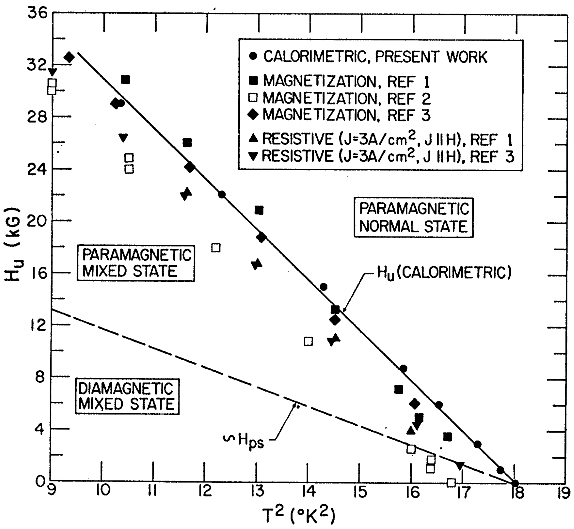

FIG. 2. Upper critical field H_u-versus-T^2 for the annealed Ti-16 at.% Mo specimen of Fig. 1 (specimen #2) represented by solid circles. Also shown for comparison are earlier magnetization and resistive determinations of $H_u(T)$ for other annealed specimens of Ti-16 at.% Mo (Ref. 1 and 3, specimen #1; Ref. 2, specimen #3). The paramagnetic onset field $H_{ps}(T)$ is the same as that determined in Ref. 1 for specimen #1 except that the straight H_{ps}-versus-T^2 line has been tilted slightly so as to pass through the point $H_u=0$, $T_c^2=18.03=4.246^2$. The solid line [H_u (calorimetric)] is the parabolic fit $H_u(T)=69.4\times10^3\times[1-(T/4.246)^2]$ kG to the calorimetrically determined $H_u(T)$.

[10] W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. **133**, A1226 (1964); J. Matricon, Phys. Letters **9**, 289 (1964).

[11] Theoretical κ_2 values assume a sepcimen demagnetizing coefficient $n=0$. For the present specimen $n\approx0.2$. However, for $\kappa\gtrsim5$ and the usual high-field reversible linear-in-H (M_S-M_N) curve, free-energy arguments suggest $H_c^2/2\approx(1/2)SH_u^2$ independent of n. Since H_u is independent of n, S and thus (by Ehrenfest's relationship) $\Delta C(T_s)$ must be nearly independent of n.

[12] The present $\kappa_2(T)/\kappa_1(T_c)$ values lies close to the Maki (Ref. 4) curve for $\beta_0^2\equiv\alpha^2/1.78\lambda_{s0}=2$, implying for the present $\alpha^2\approx3.4$, a $\lambda_{s0}\equiv\hbar(3\pi k_BT_c\tau_{s0})^{-1}\approx1$, or roughly 1 spin-flip per 100 electronic collisions ($\tau_{s0}^{-1}\equiv$spin-flip scattering frequency). Because of the extreme sensitivity near T_c of experimental and theoretical values of $\kappa_1(T)/\kappa_1(T_c)$ to the somewhat uncertain $H_c(T)/H_c$ $(T=0)$, we have chosen to compare instead experimental and theoretical values of $h^*(t)=H_u(t)/(-dH_u/dt)_{T_c}$ where $t\equiv T/T_c$, as recommended in Ref. 5. This yields $\lambda_{s0}\approx1$ on the basis of the Maki theory (Ref. 4) and $\lambda_{s0}\approx0.8$ on the basis of the WHH theory (Ref. 5). Cape (Ref. 2) deduced a $\lambda_{s0}\approx0.7$ for Ti-16 at.% Mo. A comparison of the present calorimetric κ_1 and κ_2 values with those deduced from the magnetization measurements of Ref. 3 appears in L. J. Barnes and R. R. Hake, Ann. Acad. Sci. Fennicae (to be published).

[13] C. G. Schull and F. A. Wedgwood, Phys. Rev. Letters **16**, 513 (1966); L. W. Gruenberg and L. Gunther, *ibid.* **16**, 996 (1966).